Low Temperature Carbon Monoxide
Conversion Catalysts

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The purpose of this paper is to report on the initial commercial operation of a low-temperature carbon monoxide conversion catalyst and to show some of the economic advantages of using such a catalyst in the production of hydrogen and ammonia synthesis gas.

HISTORICAL: The production of hydrogen for making ammonia synthesis gas has reached major proportions. The quantity of hydrogen used in ammonia synthesis in the U.S. last year exceeded 540 billion cubic feet, more than 1.5 billion cubic feet per day. The consumption of hydrogen for ammonia synthesis world-wide now exceeds 1500 billion cubic feet per year and is growing at the rate of somewhere between seven and ten per cent per year. In addition, the production of hydrogen for chemical hydrogenations and for hydrotreating and hydrocracking is becoming an increasingly important factor in the consumption of hydrogen. Hydrocracking along with increased ammonia production portends a continued increase in the requirements for more hydrogen production.

Most of the hydrogen being consumed is produced by the reaction of steam with a hydrocarbon

$$CxHy + xH_2O = xCO + (x + \frac{y}{2}) H_2$$
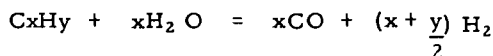
and is commonly referred to as "reforming." Smaller quantities of hydrogen are produced by the partial oxidation of hydrocarbons by the reaction

$$CxHy + \frac{x}{2} O_2 = xCO + \frac{y}{2} H_2$$
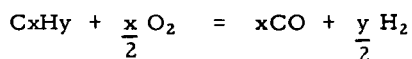
In order to maximize the quantity of hydrogen produced in these processes, it is essential to convert the carbon monoxide to carbon dioxide and additional hydrogen by reacting it with steam

$$CO + H_2O = CO_2 + H_2$$
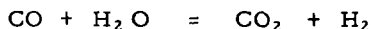
This reaction is in equilibrium and tends to go to completion towards the right as the temperature is decreased. Pressure has no effect on the equilibrium. It, therefore, becomes desirable to promote this reaction at the lowest possible temperature. In order to increase the reaction rate at which equilibrium

conditions are approached, it has been necessary to carry out the reaction in the presence of a catalyst. The catalyst used almost exclusively for this reaction for the last 40 to 50 years has been an iron oxide-chrome oxide promoted catalyst. This catalyst caused the reaction to proceed at commercially feasible rates at temperatures as low as 650°F, and it had a useful life of three to over ten years, depending on the conservatism of the design. Although other catalysts have been investigated and reported [1] [2] for promoting the reaction between carbon monoxide and steam at temperatures lower than 650°F, none have found commercial acceptance, due principally to an impractically short life when used at near atmospheric pressure. One low-temperature conversion catalyst, however, found limited commercial acceptance when used at relatively high pressures.

It was not until 1953 that a commercial plant was constructed for the production of hydrogen for the manufacture of ammonia synthesis gas by steam-hydrocarbon reforming at pressures appreciably higher than atmospheric, approximately 90 psig. Since that time most of the plants constructed operate at pressures ranging from 75 to 300 psig. The plants formerly constructed to operate at near atmospheric pressure are now being replaced or converted into plants operating at the higher pressures.

In 1931 Larson [3] was granted a patent on a catalyst for promoting the reaction between carbon monoxide and steam at temperatures as low as 540°F. A commercial plant was constructed early in the period of 1940-1950 for the production of hydrogen from water-gas for the manufacture of ammonia synthesis gas. The conversion of carbon monoxide to carbon dioxide and hydrogen was carried out over a catalyst apparently based on the Larson patent at approximately 450 psig. Although exact operating temperatures and rates have never been published, they are known to be in the range of 350° to 650°F, and space velocities of 400 to 1000 SCF per cubic foot of catalyst. Even though the catalyst had a relatively short life, it continued to be used even to the present time. This catalyst never found commercial acceptance for low pressure operation, presumably because of an impractically short life.

Catalysts and Chemicals Inc., soon after its formation in 1957, started successful development work on the adaptation of a catalyst, in general similar to the Larson catalyst, for promoting the conversion of carbon monoxide in the temperature range of 350° to 650°F. Over eight commercial charges of this catalyst, designated as C18 [4], are in operation or soon to go in operation at pressures ranging from near atmospheric to 350 psig; however, most of these plants will operate at over 100 psig. Pilot plant and commercial experience show that the catalyst will operate at rates appreciably in excess of those for the conventional iron oxide-chrome oxide type catalyst. With reasonable extrapolation of the available commercial experience, a practical life of at least one and one-half to three years can be expected.

PRINCIPAL ADVANTAGES OF C18 TYPE LOW-TEMPERATURE CONVERSION CATALYST: The advantages of a low-temperature carbon monoxide conversion catalyst in hydrogen production are obvious from a study of the equilibrium reaction

$$CO + H_2C = CO_2 + H_2$$
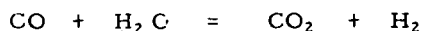
The equilibrium constant for the reaction has a value of 22 at 650°F, which is the generally accepted minimum effective temperature for the use of the iron oxide-chrome oxide catalyst. The equilibrium constant is 207 at 400°F, which is a reasonable temperature for the C18 type low-temperature conversion catalyst. The practical significance of this is that at the same steam concentration, the use of the C18 catalyst will result in over 99 per cent conversion of the carbon monoxide, whereas the iron oxide-chrome oxide catalyst will give only 90 to 95 per cent conversion at its lowest effective temperature.

If it is assumed that the processing scheme for hydrogen production for the manufacture of ammonia synthesis gas is the conventional steam-hydrocarbon reforming-- consisting of a primary and secondary reformer followed by carbon monoxide conversion, carbon dioxide removal and then methanation of the residual carbon monoxide--and that the acceptable level of residual carbon monoxide to be methanated is not more than 0.3 mol per cent, the steam requirement for achieving this degree of conversion in a single stage of carbon monoxide conversion with the usual interstage cooling is 3.5 mols of steam per mol of dry feed gas when an iron oxide-chrome oxide catalyst is used. When the C18 low-temperature conversion catalyst is used, the steam requirement is 0.7 mol per mol of dry feed gas, a reduction of 80 per cent. The greater quantity of steam required with the iron oxide-chrome oxide catalyst, however, is considered impractical and either a lower quantity of steam is used with a single stage of conversion, followed by carbon dioxide removal and methanation, or two stages of carbon monoxide conversion are used with carbon dioxide removal after each stage, followed by methanation. In the first case, the carbon monoxide to be methanated ranges from 0.6 to 1.0 mol per cent. This greater quantity of carbon monoxide not only increases the quantity of inerts in the synthesis gas, thus making the synthesis of ammonia less efficient, but for each mol of carbon monoxide methanated, 3 mols of hydrogen are consumed, requiring a larger plant to produce the expected quantity of ammonia. In the second case where two stages of conversion are used, the carbon monoxide to be methanated does not exceed 0.3 mol per cent; however, considerably more equipment is required, consisting of a stage of carbon dioxide removal, heaters, saturators, exchangers, coolers, etc., which not only increase the capital cost of the plant, but also the operating cost.

The additional steam that must be added to the gas for the second stage conversion reaction brings the over-all steam requirements to 1.4 mols of steam per mol of dry gas exit the secondary reformer. This is still twice the quantity of steam required for achieving the same degree of conversion in a single stage conversion system using the low-temperature shift catalyst.

These steam requirements for the three basic carbon monoxide conversion systems are summarized in Figure 1. Additional significance to the potential advantage of the low-temperature shift catalyst can be seen by observing on the graph that the steam level in the gas required to achieve a methane leakage of 0.2 mol per cent from a secondary reformer is 0.5 mol per mol of dry gas at 150 psig and 0.7 mol per mol of dry gas at 300 psig. It has already been indicated that the 0.7 steam to dry gas ratio is the required steam level to reach the 0.3 per cent carbon monoxide level in the feed to the methanator. Further, the practical steam levels required in the gas to supply the energy requirements of regenerating the carbon dioxide removal solution are shown for an amine system and for one of the newer carbon dioxide removal systems. These steam to gas ratios are 1.40 and 0.70, respectively.

Once again, the 0.70 value appears and shows that the C18-1 development is an important contributor to the advancing technology in ammonia synthesis gas production.

Figure 1 also shows the relative physical size of the shift converters for the three basic conversion systems. If the size requirement of the single-stage system using the C18-1 catalyst in conjunction with pre-conversion over a conventional catalyst is considered as 1, the size of the two-stage conventional catalyst system is 1.4 and for the single-stage conventional catalyst system is 6.0.

The potential advantages of the low-temperature shift catalyst in ammonia synthesis gas production are further shown in Table I, wherein a comparison is made in some of the critical conditions and requirements for a hypothetical 300 ton per day ammonia plant for the following three alternate processing schemes. The reformer pressure level in all cases is 300 psig exit the reformer tubes.

   Case 1   A single-stage conversion system employing conventional catalyst in series with low-temperature shift catalyst and using one of the newer "lower energy" carbon dioxide removal processes.

   Case 2   The same as Case 1 except employing conventional catalyst throughout the single-stage converter and operating with higher inerts in the synthesis gas loop.

   Case 3   The same as Case 2 except using amine as the carbon dioxide removal system and obtaining a greater conversion of the carbon monoxide due to the higher steam requirements of the amine system.

Comparison of the hydrocarbon requirements in the above systems in Table I indicates that the use of low-temperature shift catalyst permits the synthesis gas section of the plant to be reduced in size by approximately 12 per cent. The increased cost of the catalyst required to give this advantage is approximately $50,000, including the use of a primary reforming catalyst with the best known activity and heat transfer characteristics such that full advantage can be taken in reducing the physical size of the plant.

Figure 2 shows the relative hydrocarbon requirements for the process, including fuel and steam production, for these three systems of synthesis gas production.

The production of large quantities of relatively high-purity hydrogen, such as are necessary for the new hydrocracking of hydrocarbons processes, is gaining rapidly in industrial importance. The typical plant involves high pressure reforming, single-stage conversion, carbon dioxide removal, and methanation of residual carbon oxides. The degree of conversion of the carbon monoxide exit the reformer influences the ultimate cost of these plants since unconverted carbon monoxide ends up as a methane impurity in the product and affects the degree of reforming to reach a given product purity. The greater conversion of carbon monoxide is made possible through the use of low-temperature shift catalyst and, therefore, permits a substantial reduction in the physical size of the reformer with attendant lower steam and fuel requirements, or alternatively, permits reforming at a higher

pressure level with a subsequent reduction in compression costs.

Figure 3 shows a comparison of a reformer design when using conventional cata-
lyst versus the use of low-temperature carbon monoxide conversion catalyst
and the best reforming catalyst available. The size of the reformer in terms of
catalyst volume required and the maximum tube wall temperature in the reform-
ing furnace are plotted against hydrogen purities of 95 to 98 per cent for a
production capacity of 50 MMSCFD of net hydrogen delivered at 150 psig. It is
shown that the use of the low-temperature conversion catalyst permits a 25 to
30 per cent reduction in the size of the reformer.

For example, in the case of 95 per cent hydrogen purity, it is observed that
approximately 740 cubic feet of catalyst are required in the reformer when using
the conventional catalyst, whereas approximately 550 cubic feet are required
when using the low-temperature shift catalyst and the best reforming catalyst
available. The maximum tube wall temperature in both cases is 1670°F assuming
the same physical size of the tubes in terms of inside diameter and length in the
fired zone of the reformer. For 97 per cent hydrogen purity, when using the con-
ventional catalyst, the reformer must contain about 785 cubic feet of catalyst and
the maximum tube wall temperature required is 1720°F. With C18 catalyst in
the shift converter, the reformer size may be reduced to contain 665 cubic feet of
catalyst and the tube wall temperature required is now 1700°F.

LABORATORY DEVELOPMENT AND COMMERCIAL DEMONSTRATION OF THE
EFFECTIVENESS OF C18 LOW-TEMPERATURE CARBON MONOXIDE CONVERSION
CATALYST: Bench scale and pilot plant work have been conducted in the laboratories
of Catalysts and Chemicals Inc. to establish the preferred catalyst composition, the
best method of preparation of the catalyst, the method of reduction giving a catalyst
of the highest activity, the optimum operating conditions, the effect of poisons, and
the decline of activity with time on stream versus operating temperature. Specific
studies were made on the effect of total pressure, the partial pressure of carbon
dioxide, and the partial pressure of steam on the kinetics of the reaction.

It is not to be implied that the laboratory studies have resulted in complete answers
to the quantitative effect of all the variables involved; however, it is believed that
sufficient information is known upon which to base workable designs at the usual
processing conditions.

Life tests in excess of 13 months' duration were conducted at typical operating con-
ditions.

The first commercial charge of C18 was placed on stream on January 1, 1963 in
a 210 ton per day ammonia plant at about 120 psig. An operating mishap during
reduction of the catalyst and adverse conditions during the initial stages of opera-
tion resulted in below-normal initial activity of the catalyst. Despite these factors,
however, the catalyst had sufficient activity to show a distinct advantage over the
previous conventional catalyst, and operation has continued to the date of this
writing with no more than the anticipated decline in activity. The initial activity
and the rate of decline in activity are shown in Figure 4. This charge of catalyst
has been on stream for 12-1/2 months as of this date.

The second commercial charge of C18 catalyst was placed on stream on May 11, 1963 in a 260 ton per day ammonia plant on the West Coast. In contrast to the first charge of catalyst, the conditions of reduction and initial operation were in accordance with the recommended procedures, and this charge of catalyst is continuing to operate at an inlet temperature of 400°F, which was the initial inlet temperature. The relative activity level and decline in activity of this charge of catalyst are shown in Figure 4, and specific data are presented in Table II. The performance of this charge of catalyst has thus far exceeded the anticipated performance based on the pilot plant life tests.

A third charge of C18 catalyst was placed in operation on July 24, 1963, operating on a slip stream of a reformer effluent at 2 psig. It continues to perform satisfactorily, and the relative activity and decline in activity are shown in Figure 4. The design level of this operation, however, which was deduced from experiments at low pressure, may prove to be uneconomical in many applications. Further operating experience is required before the use of the catalyst can be encouraged at low pressures.

As stated, Figure 4 shows the performance of the C18 catalyst in these three commercial units. The relative activity with time on stream is shown in relation to the performance of the catalyst throughout the 13-month life test in CCI's pilot plant.

A projection of these curves indicates an anticipated life of the catalyst of one and one-half to three years in commercial operation. A significant factor shown in Figure 4 is the commercial verification of the importance of reduction conditions on the activity of low-temperature conversion catalysts when the performance in Plants 1 and 2 is compared.

As of this writing, five more commercial charges of C18 catalyst have been sold for startup in early 1964.

SUMMARY: The C18 low-temperature carbon monoxide conversion catalyst has been demonstrated commercially to offer a proven economical life in hydrogen and ammonia synthesis gas manufacture. The catalyst is, in general, more sensitive to both catalyst poisons and abnormal operating conditions than is the conventional iron oxide-chrome oxide catalyst and, therefore, requires more careful operation and greater attention to detail in process design. Specifically, the catalyst activity is severely affected by even trace quantities of sulfur in the feed gas. The activity is appreciably affected by the subjection of the catalyst to temperatures in excess of the normal operating level.

The C18 catalyst must be reduced under special conditions and with great care in order to obtain maximum activity and long life. [5]

Application of the catalyst in low pressure operations has not been shown to be practical, and more operating experience will be required before this can be determined.

The catalyst has been proven to offer an attractive payout factor in terms of initial plant investment and operating economy. The ultimate life of the catalyst could well exceed the projected minimum of one and one-half to three years based on the commercial operation to date.

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References:

(1)   Storch, H. H. and Pinkel, I. I., Industrial and Engineering Chemistry,
        29, 715; 1937.

(2)   White, E. C. and Schultz, J. F., Industrial and Engineering Chemistry,
        26, 95-7; 1934.

(3)   U. S. Patent 1,797,426, March 24, 1931.

(4)   Patent application pending.

(5)   Patent application pending (on reduction procedure).

TABLE I

Comparison of Process Design Features of Ammonia Synthesis Gas Manufacture Using Low-Temperature Carbon Monoxide Conversion Catalyst

Process Scheme: Steam-Hydrocarbon Reforming, Primary and Secondary; 300 psig; Carbon Monoxide Conversion; Carbon Dioxide Removal; Methanation of Carbon Oxides.

Basis: 300 Tons Per Day Ammonia

Case *	1	2	3
CO in Shift Converter Effluent**	0.2 mol per cent, dry basis	1.1 mol per cent, dry basis	0.5 mol per cent, dry basis
Inerts (CH_4 + A) Exit Methanator, mols/hr	29.89 (0.96 mol per cent)	70.85 (2.1 mol per cent)	38.30 (1.21 mol per cent)
Synthesis Gas Required for 300 TPD NH_3			
mols/hr	3114.98	3361.01	3165.46
Relative Amount	100%	107.9%	101.6%
Hydrocarbon, mols/hr			
Process Requirements	702.44	788.11	720.68
Fuel Requirements	295.63	331.68	451.77
Total Requirements	998.07	1119.79	1172.45
Relative Amount	100%	112.2%	117.47%
Air, mols/hr			
Process Requirements	988.47	1054.25	1001.99
Fuel Requirements	2957.70	3318.42	4519.74
Total Requirements	3946.17	4372.67	5521.73
Relative Amount	100%	110.81%	139.93%
Steam Requirements			
Total Lbs/Hr	69,570	75,200	114,350
Relative Amount	100%	108.1%	164.4%
Relative Reformer Size	100%	112.9%	103.0%
Relative Shift Converter Size	100%	125.1%	194.6%

* Cases are defined in text.
** Practical level of carbon monoxide in shift converter effluent using the steam requirements of the carbon dioxide regeneration system to full effectiveness in the shift converter.

Table II Plant Operating Data; C18 Low-Temperature Carbon Monoxide
Conversion Catalyst (260 Tons/Day Ammonia Plant, 120 PSIG)

Date	Days on Stream	Dry Gas S. V. SCFH/ V/Hr.	Inlet Temp. °F	Outlet Temp. °F	Inlet S/G Ratio	Gas Analyses, Mol Per Cent					
							CO_2	CO	H_2	CH_4	$N_2 + A$
5-24-63	13	1925	410	445	0.336	In	4.2	3.0	71.4	0.2	21.2*
						Out	7.0	0.02	72.4	0.2	20.38*
6-27-63	47	1980	400	450	0.42	In	0.8	3.0	74.0	0.3	21.9
						Out	3.8	0.06	74.0	0.3	21.8
9-4-63	116	1800	402	453	0.38	In	0.11	3.16	71.76	0.27	24.70
						Out	2.91	0.06	72.97	0.27	23.80
12-4-63	207	1840	405	456	0.388	In	0.23	3.10	75.69	0.28	20.70
						Out	3.18	0.05	76.40	0.27	20.10

*Analyses by customer's laboratory. Nitrogen and argon by difference.
All other analyses by CCI chromatograph and were essentially confirmed
by customer analyses.

Figure 1 - Low Temperature CO Conversion Catalyst (C18)

A - Low Temperature Catalyst
B - 2-Stages Conventional Catalyst
C - 1-Stage Conventional Catalyst

Relative Catalyst Volumes

S/G Levels Required For:

Amine Regeneration

Sulfinol Regeneration and
0.2% CH_4 at 300 PSIG

0.2% CH_4 at 150 PSIG
(Exit Secondary)

Relative Steam and Catalyst Requirements for Conversion of CO
in Secondary Reformer Effluent to 0.3% CO Inlet Methanator
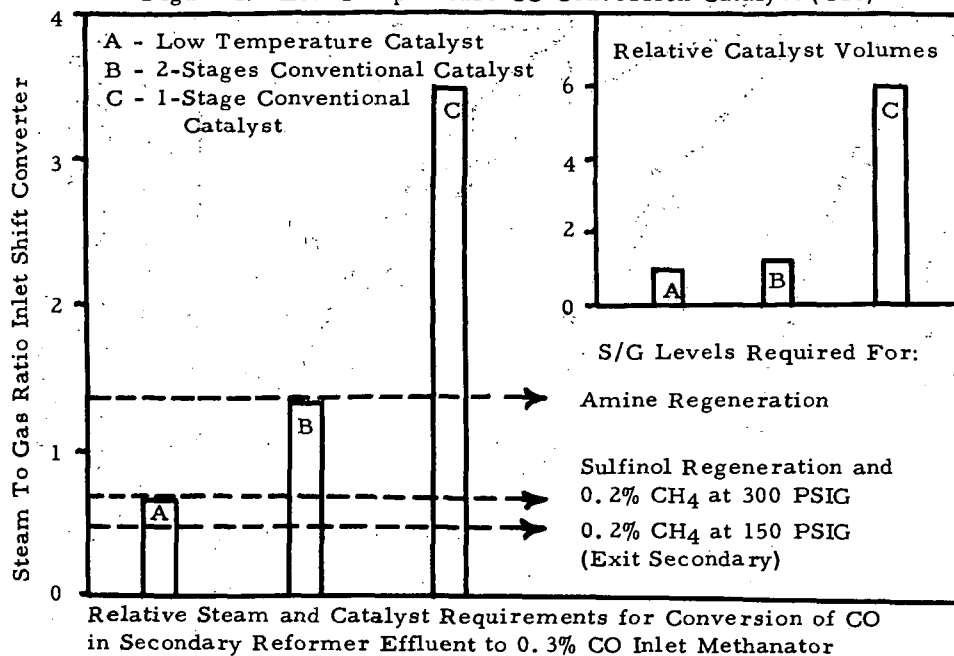
Figure 2 - Low Temperature CO Conversion Catalyst (C18)

Case 1
(3947)

Case 2
(4373)

Case 3
(5522)

Process Total

Case 1-Low Temperature Catalyst and Sulfinol

Case 2-One Stage Conventional Catalyst and Sulfinol

Case 3-One Stage Conventional Catalyst and Amine

Mols/Hour CH_4 Required for 300 Tons/Day NH_3 at 300 PSIG
Reforming

Figure 3 - Low Temperature CO Conversion Catalyst (C18)

50 MMSCFD Net H_2
150 PSIG Reforming

Maximum Tubewall Temperature in Reformer

1850° 1800° 1750° 1700° 1650°

Conventional Catalyst

Low Temperature Conversion

Low Temperature

Conventional

Per Cent H_2 Product Purity

98%   97%   96%   95%

Volume Catalyst Required in Reformer

800 c.f.   700 c.f.   600 c.f.   500 c.f.   400 c.f.

Influence of Low Temperature CO Conversion
Catalyst on Size of Reformer and Maximum
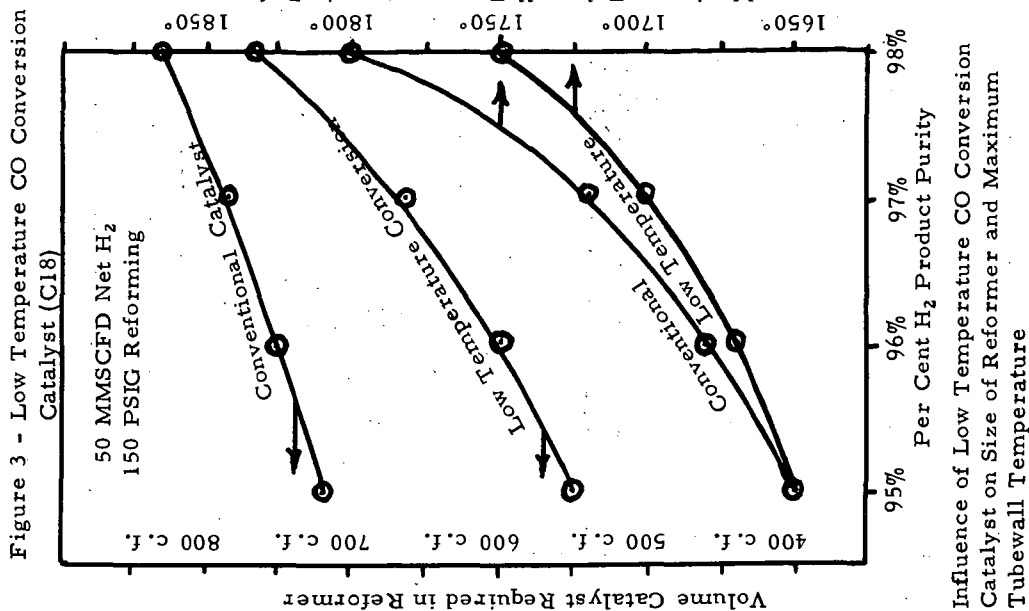Tubewall Temperature

Figure 4 - Low Temperature CO Conversion Catalyst

Commercial Performance of C18
and Life Test Results

Relative Activity C18, Per Cent of Design

400

300

200

100

Plant 2 - 120 psig

Plant 3 - 2 psig

CCI Life Test - 150 psig

Plant 1 - 120 psig

Time on Stream (Months)

0   2   4   6   8   10   12   14   16   18   20   22